Simple Physically Based Equations of State

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Calculations of thermodynamic properties of pure substances and mixtures are usually performed with equations of state. The approaches to equations of state range from theoretical models for molecular fluids to empirical equations. In physically based models the parameters describe certain molecular properties which makes it possible to extrapolate the thermodynamic properties over temperature, pressure and also homologous series. Empirical cubic equations of state are often preferred in industrial applications because of their mathematical simplicity. Such equations can give no more then three roots if the molar volume is calculated for a given pressure and temperature. These roots can be immediately identified with the liquid, the gas phase and the unstable solution. Besides application arguments, there are physical reasons for developing mathematically simple equations. Investigations of the global phase behavior have shown, that even simple physically-based model equations can produce complex phase behavior which was usually related to more complicated molecular models [1]. As a consequence, equations of state should be mathematically simple in order to avoid undesired phase diagrams [2].

Recently, we developed a simple theoretical fourth-order equation of state for the hard-sphere fluid [3]. A generalized form of this equation was employed for mapping of complicated model equations derived with perturbation approaches. For fourth-order equations one can calculate the molar volume analytically similar to cubic equations. Hence, the fourth-order mapping equation combines mathematical simplicity with physical background. The mapping is applied to a model for chain molecules [4] which was derived within the thermodynamic perturbation theory and a dipole-equation [5] which was derived within the Pople expansion. The results are biquadratic equations for chain molecules [6] and dipolar molecules [7]. Special attention has also been paid to the description of the near-critical region. Current work focuses on the simplification of a recent model [8] for the near-critical region.

[1] L.V. Yelash and T. Kraska, *Ber. Bunsen-Ges. Phys. Chem.* **102**, 213 (1998); *Z. Phys. Chem*. **211**, (1999).
[2] J.H.M. Levelt-Sengers, *Fluid Phase Equil.* **158,** 3 (1999).
[3] L V. Yelash, T. Kraska, and U.K. Deiters, *J. Chem. Phys*. **110**, 3079 (1999).
[4] W.G. Chapman, G. Jackson, and K.E. Gubbins, *Molec. Phys*. **65,** 1057 (1988).
[5] G.S. Rushbrooke, G. Stell, and J.S. Hgtye, *Molec. Phys*. **26**, 1199 (1973).
[6] L.V. Yelash and T. Kraska, *Phys. Chem. Chem. Phys*. **1**, 2449 (1999).
[7] L.V. Yelash and T. Kraska, submitted.
[8] K. Leonhard and T. Kraska, *J. Supercritical Fluids* **16**, 1 (1999).